

# Molecular Dynamics Simulation of Electron Trapping in the Sapphire Lattice

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Energy storage and release in dielectric materials can be described on the basis of the charge trapping mechanism. Most phenomenological aspects have been recently rationalized in terms of the space charge model [1,2]. Dynamical aspects are studied here by performing Molecular Dynamics simulations. We show that an excess electron introduced into the sapphire lattice ( $\alpha\text{-Al}_2\text{O}_3$ ) can be trapped only at a limited number of sites. The energy gained by allowing the electron to localize in these sites is of the order of 4-5 eV, in good agreement with the results of the space charge model. Displacements of the neighboring ions due to the implanted charge are shown to be localized in a small region of about 5 Å. Detrapping is observed at 250 K. The ionic displacements turn out to play an important role in modifying the potential landscape by lowering, in a dynamical way, the barriers that cause localization at low temperature.

## INTRODUCTION

Recent theoretical and experimental efforts have focused on the mechanism of electron trapping in dielectric materials. The space charge model [1,2] based on the concept of polaron [3] has been developed to explain trapping and its consequences from an energetic point of view. The main underlying idea is that electrons trapped into the lattice build up a space charge simultaneously generating a mechanical deformation (polaron). Energy is stored both in electrostatic (coupling) and in mechanical (internal) forms [4]. Beyond a critical concentration of trapped electrons, dielectric breakdown or flashover occurs. The mechanical part of the energy is then released in the form of a thermal shock wave that produces a local heating large enough to create a plasma, eventually leading to the rupture of the material. One of the main consequences is that dielectric breakdown would not arise because of an external driving force (e.g. a high voltage difference between the electrodes), but because of the internal stress caused by the accumulation of the trapped charges. Thorough investigations have shown that electrons can be trapped in a lattice as soon as a local variation of the dielectric susceptibility occurs. This variation can be either due to defects (vacancies, impurities, interfaces, etc...) or to crystallographic dissymmetry. Once the charge is trapped the lattice is distorted and polarized. The energy involved in this process has been evaluated within some realistic approximation, and it has been shown that an energy of at least 5 eV is stored upon electron trapping.

On the other hand, trapping has been studied experimentally using the mirror method [5,6]. It has been shown that trapping can occur in pure sapphire ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub> single-crystals) only for temperatures lower than 250 K, but the trapping/detrapping dynamics in this kind of materials is not yet fully understood. In particular, the dynamic behavior in the range of pico-second to femto-second cannot be observed in real experiments, while it is crucial to elucidate the charge trapping mechanisms. In this work we apply Molecular Dynamics technique (MD), which has widely proven efficiency in reproducing the properties of real materials [7], to explore these aspects of electron trapping in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Ionic polarization has been described in terms of a shell model which is briefly outlined in the following section. We then show how the solvated electron can stay firmly in some specific lattice sites at low temperature producing a local polarization and how, despite the fact that the potential turns out to be quite deep, the electron can self-detract at moderate temperatures.

## SHELL MODEL AND DETAILS OF THE SIMULATION

The potential used for corundum was based on the assumption of a fully ionic model [8]. Ionic polarization was introduced through a modified shell model. In the shell model introduced by Dick and Overhauser [9], each ion is represented by a massive core and a massless shell which simulates the valence electrons. The total ionic charge divides amongst core and shell, the core-shell interactions being described by harmonic springs. In this work we use a modified shell model due to Catlow and Stoneham [8].

The assumption of massless shells is a way to introduce the adiabatic (Born-Oppenheimer) approximation in the context of the shell model. It means that shells have to adjust instantaneously to the present configuration of the cores. This implies that a full relaxation of the shells is needed at each step of the MD simulation. In practice, full relaxation is very difficult and costly to achieve, but if a less strict convergence is required, a systematic error is accumulated during the simulation that unphysically damps the motion of the cores [10]. The slight inconsistency between force and energy translates into a continuous and systematic energy loss. To avoid this problem we adopted a Car-Parrinello-like strategy by assigning a small, but finite mass to the shells, and by treating them as dynamical variables evolving according to their own (fictitious) equations of motion [11]. This approach proved to be very efficient in the context of ab initio MD, and the reason is that a second order dynamics for the shells gives rise to oscillating fictitious forces on the cores that average out during the slow dynamics of the cores. We have chosen a mass of 10% the proton mass, so ensuring energy conservation to high accuracy. The Coulombic contribution to the interionic potential is calculated by the Ewald summation technique [12,13]. Non-Coulombic, short-range interactions between shells are described by the Buckingham potential [14], i.e.

$$V_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C_{ij}}{r_{ij}} \quad (1)$$

The sets of parameters  $A_{ij}$ ,  $C_{ij}$ , and  $\rho$  for each pair of ionic species are displayed in Table I, and the values of the spring constant and the partial charges for cores and shells in Table II. All values have been taken from Ref. [15], except for the Al<sup>3+</sup> core-shell spring constant which was adjusted to fit the dielectric constant of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> computed from the simulation to the experimental value ( $\epsilon_r = 9.8$ ).

The simulation has been performed on a system of 120 ions at constant number, volume and temperature (canonical ensemble). We have placed the particles into an orthorhombic simulation box of experimental lattice constants, and replicated using periodic boundary condi-

tions. Verlet algorithm was used to integrate the equations of motion. A time step of 0.1 fs had to be used in order to integrate properly the equations of motion for the shells, due to their small mass. Simulations were started with all ions at their equilibrium positions, and velocities taken at random from a Maxwell-Boltzmann distribution at the desired temperature. Before simulating the charge trapping we have verified the accuracy of the model on reproducing the physical properties of pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, namely the lattice energy and the mean square displacement. We have found a value of -160 eV at  $T = 300\text{ K}$ , compared to -160.4 eV from experiment [16] and -160.24 eV from Catlow and al. [15]. The mean square displacement also compared reasonably with experimental measurements at 300 K and 2170 K [17], as shown in Figs. 1 and 2. These results obtained with our modified shell model gave us confidence to continue the study of charge trapping by introducing an excess electron into the corundum  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> lattice.

## TRAPPING SIMULATION

The lattice of alumina can be described as a succession of anionic and cationic planes with hexagonal in-plane ordering. The O<sup>2-</sup> ions form an hexagonal compact stacking, slightly distorted in order to make room for the larger Al<sup>3+</sup> ions. All sites of the crystallographic arrangement are non-equivalent [18]. We first run the simulation for a perfect crystal of 120 ions for 10000 time steps (equal to 1 ps) to ensure thermal equilibration. To obtain a hint on possible trapping sites we have computed the (unrelaxed) potential energy surface at the (001) plane that contains the O<sup>2-</sup> ions.

### Potential energy surface

The potential of the uncharged lattice at a generic point (x,y) in the (001) plane is given by the Coulomb interaction between the ions in the crystal and a test particle of charge unity placed at that point. Since the test particle is a hypothetical object, the potential has to be computed with all ions in the equilibrium positions of the uncharged lattice. The resulting surface is shown in Fig. 3. It can be observed the existence of local minima where the electron can be trapped. We have chosen the position of one of these potential wells as the initial position for the excess electron in our simulation.

### Model for the ion-electron interaction

In this first approach to the problem of electron dynamics in dielectrics we have considered the electron as a

purely classical particle. The interaction potential between the electron and O<sup>2-</sup> was modelled by a pure Coulomb repulsion at all distances.

$$\Phi_{eO^{2-}}(r) = \frac{Z_je^2}{r} \quad \text{for core and shell} \quad (2)$$

The e<sup>-</sup>-Al<sup>3+</sup> interaction was instead described in terms of short-range repulsion, as though the excess electron was an oxygen shell, but of charge unity and finite mass (the electron mass).

## RESULTS

We have performed simulations at several different temperatures up to 300 K. Fig. 4 shows the path of the (classical) electron at 300 K, and Fig. 5 corresponds to 200 K. Also the potential energy surface in the (001) plane is shown in the plots. In Fig. 6 we plot the mean square distance traveled by the electron as a function of time. It is clearly apparent that at 300 K the electron escapes from the initial trapping site, while at 200 K it stays close to the bottom of the potential well. The transition from one regime to the other has been located around 250 K. Below this temperature the excess electron solvates, and above it jumps from one well to another. These results are in good agreement with experimental data obtained by the mirror method [4].

In no case the kinetic energy of the ions is sufficient to overcome the barriers present, but at high temperatures the ions in the polarization cloud can respond more rapidly by lowering the barriers in a dynamical way. Indeed, the active presence of the excess electron has an important backreaction effect onto the neighboring ions. When the excess electron is trapped, it attracts the positive Al<sup>3+</sup> ions and repels the negative O<sup>2-</sup> ions causing a lattice distortion and a dielectric polarization.

Despite the limited size of our system we have been able to determine the main features and magnitude of the ionic displacements. The six nearest oxygen ions moved significantly outwards, away from their equilibrium positions, typically between 0.17 and 0.27 Å. The displacement pattern of the Al<sup>3+</sup> ions is more complicated. The two first neighbors are very stable, with an average vibration of 0.025 Å. This is because these two ions are strongly attracted towards the trapped electron, and hence they behave as though their mass were renormalized by the interaction. The next two Al<sup>3+</sup> neighbors are also largely attracted towards the trap, because the outwards motion of the O<sup>2-</sup> ions leaves enough place for them to move in. The average fluctuation of the Al<sup>3+</sup> ions is about (0.07 ± 0.01) Å. The outer Al<sup>3+</sup> ions do not experience any significant force, as a consequence of the short range of the e<sup>-</sup>-Al<sup>3+</sup> interaction. According to this pattern of distortions, we estimate the size of the polaron in about 4.8 Å.

We have computed the potential energy surface for the charged lattice at  $T = 200\text{ K}$ , and we show it in Fig. 7 compared to the uncharged potential. The former was calculated with the ions in their displaced positions after the introduction of the excess electron, but only the potential felt by the test charge was computed, in order to compare with the uncharged lattice. The bottom of the potential well turns out to be 4.7 eV lower in energy in the case of the deformed (charged) lattice. Therefore, the effective presence of the electron further stabilizes the trap by increasing the depth of the potential well. These results are consistent with experiments showing that the energy necessary to detrap charging electrons is larger than the energy gained upon trapping them [5]. The total energy of the lattice increases about 4-5 eV upon electron implantation, so that this number represents the energy of formation of the polaron in  $\alpha\text{-Al}_2\text{O}_3$ . This value is consistent with the estimation done using the space charge model [1]. Part of the energy is stored as mechanical energy and, when dielectric breakdown occurs, it is supposed to be released in the form of a shock thermal wave that eventually leads to fracture.

## CONCLUSIONS

In this paper we have investigated the phenomenon of electron trapping in the corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) lattice. Our simulation revealed that electrons can only be trapped at temperatures lower than  $T_d = 250\text{ K}$ . This is in good agreement with experimental results obtained using the mirror method. Trapping turns out to be possible only at lattice sites where the potential surface of the uncharged lattice exhibits a minimum. This is in agreement with the space charge model, as these sites appear to be polarizability defects due to crystallographic dissymmetry. Although our simulations reproduce the main features of electron trapping at a semiquantitative level, further improvement is needed in two directions: (a) modelling of the short-range interaction of the electron with the ionic species, and (b) quantum treatment of the electronic dynamics. Work is in progress along these two lines.

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## TABLE CAPTIONS

**Table I:** Values of the parameters used for the short-range interactions (\* values from Catlow et al. [8]).

Interactions	$A_{ij}$ (eV)	$\rho$ ( $\text{\AA}^{-1}$ )	$C_{ij}$ (eV $\text{\AA}^6$ )
Al-Al	0*	0.1*	0*
O-O	22764*	0.149*	27.88*
Al-O	1460.3*	0.29912*	0*

**Table II:** Values of the parameters used for the shell model (\* values from Catlow et al.. [8]).

Parameters	$\text{Al}^{3+}$	$\text{O}^{2-}$
spring constant (eV $\text{\AA}^{-2}$ )	924.88	103.07*
core charge (e)	1.6170*	0.8106*
shell charge (e)	1.3830*	-2.8106*

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FIG. 1. Mean square displacement for the  $\text{Al}^{3+}$  ions at  $T=300\text{ K}$  and  $T=2170\text{ K}$ . The curves are scaled by a factor  $x = 0.01$  and  $x = 0.1$ , respectively.

FIG. 2. Mean square displacement for the  $O^{2-}$  ions at  $T=300\text{ K}$  and  $T=2170\text{ K}$ . The curves are scaled by a factor  $x = 0.01$  and  $x = 0.1$ , respectively.

FIG. 3. Potential surface for the uncharged lattice.

FIG. 4. Path of the excess electron at  $T = 300\text{ K}$ .

FIG. 5. Path of the excess electron at  $T = 200\text{ K}$ .

FIG. 6. Mean square displacement of the electron at  $T = 300\text{ K}$  and  $T = 200\text{ K}$ .

FIG. 7. Comparison between the potential surfaces of the uncharged lattice and the charged one.













